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Emerging membranes for electrochemical systems: (I) solid polymer electrolyte membranes for fuel cell systems

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Abstract: Solid Polymer Electrolyte Membranes (SPEMs) play a vital role in polymer electrolyte fuel cell systems. The high cost (US\$70-150/ft²) and/or poor performance of the existing membranes prompted many industrial and university research groups world-wide to develop very specific and low cost (US\$2-50/ft²) polymer-based electrolyte membranes. This paper is discussing progress on these key topics and the openings for the future. The advantages and disadvantages of the already developed perfluorinated ionomer membranes (Nafion, Flemion, Aciplex, Dow or Asahi Chemical) are described. The development of SPEMs during the last ten years is investigated and analysed in terms of methods of preparation, properties and potential uses in polymer electrolyte fuel cell systems. The SPEMs, which are in development, has been classified as perfluorinated polymer, partially perfluorinated polymer and non-perfluorinated membranes. The advantages and disadvantages for each type of SPEMs are addressed. The openings for industrial applications of the various SPEMs are discussed including their limits and the future studies which may be done to improve their performance in practical systems.

Key words: New membranes, fabrication, performance, cost, fuel cell systems, electrochemical systems.

1. INTRODUCTION

Solid Polymer Electrolytes Membranes (SPEMs) play a vital role in acid water electrolysis [1-2] and in Solid Polymer Electrolyte Fuel Cell Systems (SPEFCs) [3-5]. The properties desired for their use as a proton conductor in SPEFCs include: a) chemical and electrochemical stability in the system operating conditions; b) mechanical strength and stability in the operating conditions; c) chemical properties of components compatible with the bonding requirements of the SPEFCs; d) extremely low permeability to reactant species to maximize coulombic efficiency; e) high electrolyte transport to maintain uniform electrolyte content and to prevent localised drying; f) high proton conductivity to support high currents with minimal resistive losses and zero electronic conductivity; and g) production costs compatible with the application.

Up to now, the Nafion® membrane and the Dow® membrane have been almost the only advanced membranes among the most effective and available that are used in practical systems. The performance of the Dow® membranes is superior to that of Nafion® 117, the major disadvantage of these membranes being their high cost (at least about US\$780/m²) [6]. This is due to the long process of preparation and to the thickness of these membranes [7]. In a recent cost/performance study [8], it has been shown that the following reduction quotients were considered suitable in fuel cell systems for public transportation: catalyst: 1/20, labour (by automation): 1/10, plates and materials: 1/10. During the last ten years, many industrial and university research groups world-wide have been developing very low cost (US\$2-50/ft²) polymer-based electrolytes for fuel cell applications.

On the other hand, Solid Polymer Electrolytes (SPEs) have received considerable attention over the last 20-25 years owing to their wide applicability to batteries, sensors or electrochromic devices [9-18]. Most commonly, they consist of polymers such as

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Polyethylene oxide (PEO) or polypropylene oxide (PPO) in which ionic salts are dissolved. These key topics will be presented in a forthcoming paper. The following paper will discuss progress on emerging membranes in Polymer Electrolytes Fuel Cell Systems and the openings for the future.

2. THE PERFLUORINATED IONOMER MEMBRANES

2.1. Case of membranes based on strong acid functions like perfluorosulfonic acid (PFSA) (Nafion®, Flemion®, Aciplex® and Dow®)

The Nafion® membrane is an example of this type of membranes. Classically, the Nafion® membranes are chemically synthesised in four steps according to the DuPont de Nemours process [7]: a) the reaction of tetrafluoroethylene with SO₃ to form the sulphone cycle; b) the condensation of these products with sodium carbonate followed by copolymerisation with the tetrafluoroethylene to form an insoluble resin; c) the hydrolysis of this resin to form a perfluorosulfonic polymer and d) the chemical exchange of the counter ion Na⁺ with the proton in an appropriate electrolyte. This membrane was introduced by DuPont in 1966.

The development of perfluorinated membranes by DuPont in the 1960's has played a vital role in electrochemical system applications. The Nafion® family of perfluorinated ionomer membranes best met the requirements for electrochemical systems (chloroalkalin, fuel cell, and other non fuel cell applications). A lifetime of over 60000 hours has been achieved at 80°C. Their general formula is given by [19] (Fig. 1a). In Fig. 1a, the values of x, y and z are x = 6-10; y = z = 1 respectively. The values of x, y, and z can

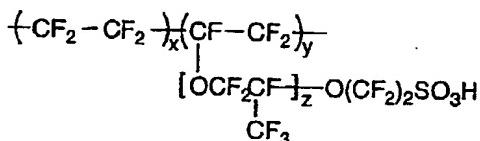


Fig. 1a. The general structure of the Nafion® membrane: X = 6-10; y = z = 1.

be varied to produce materials at different equivalent weights (EWs) and pendant chain lengths, the equivalent weight being the number of grams of polymer per mole of fixed SO₃ sites. The same features are observed with the Asahi membrane which is based on a weak-acid function (Fig. 1b) (see 2.2). The standard materials were Nafion® 120 (1200 EW, 10 mils thick) followed by Nafion®

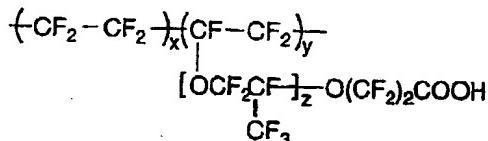


Fig. 1b. The general structure of the Asahi chemical membrane. X = 6-8, y = 0-1 and z = 1.

117 (1100 EW, 7 mil thick). The specific conductance of the 1100 EW polymer was 0.081 Ω⁻¹ cm⁻¹ [19].

These high EWs have limited the use of perfluorinated membranes in fuel cells because they lowered their power density. This was overcome with the development of the low EW perfluorinated membrane produced by the Dow® Chemical Company in 1988. The Dow® membrane is prepared by the co-polymerisation of tetrafluoroethylene with a vinyl ether monomer. The polymer can be described as having a Teflon-like backbone structure with a side chain attached via an ether group. This side chain is characterised by a terminal sulphonate functional group. The properties of the material regarding to fuel cell performance are believed to be related to side-chain length. Fig. 1c shows the structure of the Dow® membrane. As may be seen, the Dow® side chain is shorter with x = 3-10 and y = 1 and z = 0. Thus, the Dow® membrane is structurally and morphologically similar to the Nafion® membrane, but they differ with respect to their EWs, which are typically in the 800 to 850 range, and they have shorter size chains (z = 0 for Dow® and z = 1 for Nafion®) [20]. The Dow® membranes are a short side chain perfluorinated ionomer whereas the Nafion® membranes are the long side chain perfluorinated ionomer. The specific conductance of 800 and 850 EW experimental membranes has been reported as 0.20 and 0.12 Ω⁻¹ cm⁻¹ respectively [21]. It must be pointed out that the Dow® monomer is more complicated to elaborate than the DuPont monomer. The synthesis of the Dow® epoxy (see Fig. 1d) [22] is more complicated than that of the Nafion® epoxy (Fig. 1e) [23] which is a commercially available material [19].

Testing the Dow® membrane during 1987 and 1988 in Ballard fuel cells resulted in dramatic increases in SPFC performance levels [24-26]. The best 1988 performance of Nafion 117 in a six cell MK 4 stack was 0.5 V at 1400 A/ft², whereas the best performance of the Dow® membrane was as high as 0.5 V at 5000 A/ft².

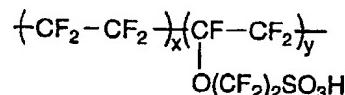


Fig. 1c. The general structure of the Dow® membrane: X = 3-10; y = 1 and z = 0.

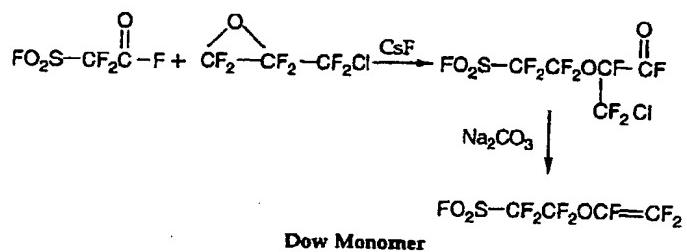


Fig. 1d. The principle of the preparation process of the Dow® membrane according to B.R. Ezzell, W.P. Carl, and W.A. Mod, U.S. Patent 4,358,412 (1982) and from [19].

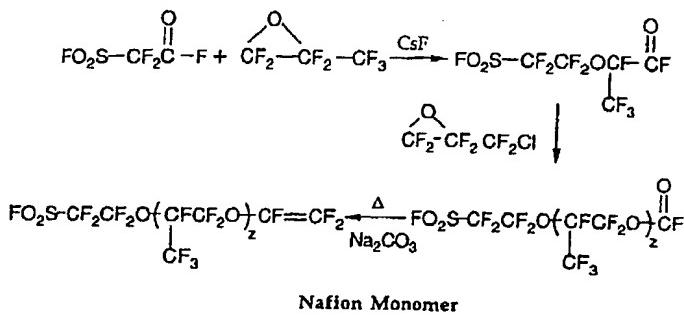


Fig. 1e. The principle of the preparation of Nafion membrane according to D.J. Connolly and W.F. Gresham, U.S. Patent 3,282,875 (1966) and from [19].

Since this success by Dow[®], DuPont has been active in developing their membranes with respect to durability and continuous improvement. They increase power densities by further decreasing the equivalent weight, from 1100 EW (Nafion[®] 115) to 1000 EW (Nafion[®] 105) and the membranes thickness from 7 to 5 mils. Nafion[®] 115 (5 mils) and Nafion[®] 105 (5 mils) are the latest materials developed specially for fuel cell applications. Single cell performance data of the Nafion[®] 105 membrane are compared with those of the BAM3G membrane (see below) and the best membranes commercially available, including Aciplex-S[®] (1000 EW, 5 mil), a long-chain perfluorosulphonic acid membrane produced by Asahi Chemical (Fig. 2). The evaluation was carried out on the MKSE (0.25 ft² active cell area) (Fig. 2) and on the experimental automotive cell (0.5 ft²) [19] (Fig. 3). The Nafion[®] 105 membranes showed performances comparable to those of the Dow[®] membrane. At the reference voltage of 0.684 V, it was shown elsewhere [27] that Nafion[®] 115 increased current capability by over 40% compared to Nafion[®] 117. But, in comparison to Nafion[®] 115, the Dow[®] membrane increased current density twofold at a cell voltage of 0.684 volt. From Figure 3, it was also claimed that the performance of the BAM3G membranes is comparable and, over 700 A/ft², better than that of the perfluorinated membrane. A perfluorinated ionomer membrane has also been developed by the Asahi Glass Company and commercialised as Flemion[®].

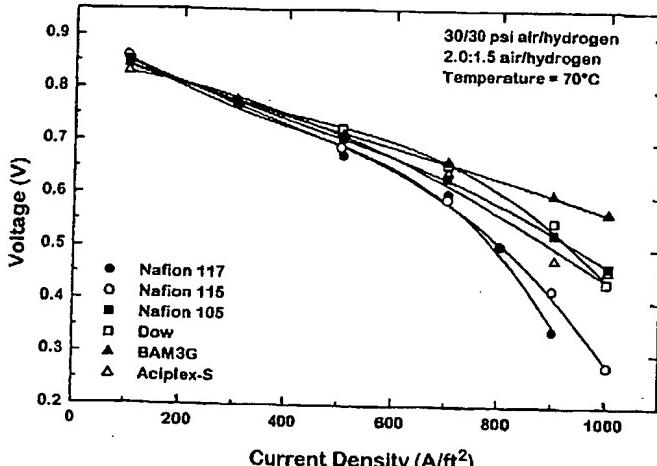


Fig. 2. Polarisation data for MKSE single fuel cell for different membranes. From [19].

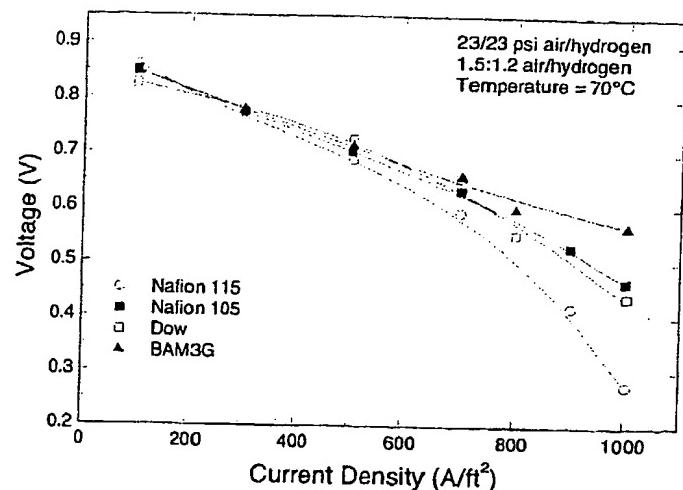


Fig. 3. Polarisation data from an automotive experimental fuel cell. From [19]

The general properties of the long-side-chain perfluorinated ionomer membranes (e.g. Nafion[®]/Flemion[®]/Aciplex[®]) and the short-side-chain perfluorinated ionomer membranes (e.g. Dow[®]) are shown in Table 1: a) EW range = 800-1500; b) conductivity = 0.20 S/cm²-0.05 S/cm² (for example, conductivity 1100 EW = 0.10 S/cm and conductivity 850 EW = 0.15 S/cm).

Nowadays, the long-side-chain above perfluorinated polymer electrolytes have been proven to have a prolonged service life under electrolysis and electrosynthesis and in fuel cell systems [28-30]. Up to now, there is no large-scale industrial electrochemical systems using the Dow[®] membranes. However, most of the perfluorinated membranes have expensive and difficult process. These membrane conductivities are also very sensitive to water management in the electrochemical systems. When they are subjected to temperatures above 100°C at atmospheric pressure, their conductivity decreases significantly due to their dehydration. Then, they are not efficient for high temperature ($\geq 150^\circ\text{C}$) electrochemical systems as water electrolysis or fuel cell systems working at this temperature range.

Table 1. Properties of perfluorinated ionomer membranes e.g. Nafion[®]/Flemion[®]/Aciplex[®]/Dow[®]

EW range	800-1500
Conductivity range (S/cm)	0.20-0.05; for example: 400 EW = 0.10 and EW 850 = 0.15
Conductance range S/cm ²	2-20; for example: 1100 EW (7 and 2 mils membrane) = 5 and 17 respectively
Dimensional stability	10-30% expansion X and Y direction from 50% RH liquid water (25°C). For example 100 EW = 16% expansion
Proven lifetime	> 50000 hours for Nafion [®] ; Flemion [®] and Aciplex [®] ; > 10000 hours for Dow
Thickness (μm)	250-50

On the other hand, the presence of the electrolyte crossing over the membranes during the electrochemical processes can be responsible in the decreasing of the cathodes potential. It is, for example, the case of high temperature ($\geq 150^{\circ}\text{C}$) methanol fuel cell systems for the perfluorinated membranes are found to be not very suitable. Due to their high price (at least US\$790/m² [6] or US\$70/ft² for Nafion® and US\$150/ft² for Dow® [19]) they may also not be appropriate for low power (15 to 100 watts) and low price electrochemical systems. If one wants to improve these membranes it is necessary to investigate new approaches for the elaboration of these membranes. These new methods may improve the conductivity of the membranes and lead to a decrease of their cost.

Although, some efficiencies have been gained by lowering the membrane equivalent weights (EW), the main improvement advantages in fuel cell performance were realised by simply thinning the membranes [31,32]. The advantages gained with this simple strategy include lower membrane resistance, lower material utilisation (and obvious related to costs savings), and improved hydration of the entire membrane. However, there is a limit to the extend to which such membrane can be thinned because of difficulties with durability and reactant crossover. W.L. Gore and Associates, Inc. proposed to solve some of these difficulties using perfluorinated ionomer membranes reinforced with woven polytetrafluoroethylene (PTFE) (see 3.1.1.).

2.2. Case of perfluorinated membranes based on weak-acid functions

This type of membrane has been developed by Asahi Chemicals (Japan). They are based on the weak function acid (-COOH) ($\text{pK}_A = 3$). The general structure of the ionomer is shown in Fig. 1b). In Fig. 1b, the values of x, y, z are $x = 6\text{-}8$; $y = 0\text{-}1$ and $z = 1$. Their equivalent weight is similar to the above membranes. The exact process of the membrane is not indicated. They have been developed for the chlor-alkali industry where they are used in a bilayer membrane. These membranes are those where a strong acid membrane (-SO₃H) ($\text{pK}_A < 1$) is coated on one side and the second side is coated with a thin layer of weak-acid membranes. Only strong-acid membrane is exposed to the anolyte so that acid may be added while the weak-acid-layer is exposed to the catholyte to prevent sodium hydroxide transport from catholyte to anolyte. These bilayer membranes are produced by several techniques including lamination, grafting and chemical conversion of some of the sulphonate acid groups to carboxylate groups. The chemical control allows good control of the gradient of the change in chemical composition. The application of the carboxylate groups based perfluorinated membranes for fuel cells was not indicated. This is probably due to the low water content, ionic conductivity and current density they can offer when used in fuel cells. The comparison of membrane properties between (-SO₃H) and (-COOH) ion exchange groups has shown that the water content and the ionic conductivity of the (-SO₃H) based membranes are higher than those of the (-COOH) based membranes. Therefore, the latter are less suitable for fuel cell applications.

3. RECENT DEVELOPMENTS IN SPEMS (SOLID POLYMER ELECTROLYTE MEMBRANES)

3.1. Solid polymer electrolyte membranes based on perfluorinated polymers

3.1.1. Perfluorinated ionomer composite membranes

Perfluorinated membranes reinforced with woven polytetrafluoroethylene (PTFE) are used in many industrial electrochemical (such as Nafion® 324 or 417). Unfortunately, the relatively coarse weave of the woven PTFE reinforcements results in membranes that are much too thick for high electrochemical performance. Since some non-woven PTFE/perfluorinated ionomer composite membranes have been formulated for ion transport studies [33,35] and for investigations of other properties relevant to chloralkali [36,37] and fuel cell [38] applications, advancements in materials and processing technology have resulted in the introduction of PTFE/perfluorinated ionomer composite membranes claimed by Gore and Associates, Inc. under the Core Select trademark. Most types of ion exchange membranes contain some type of reinforcements because they are weak and they tend to swell substantially as they incorporate a solvent into their structure. This reinforcement can be a "macro-reinforcement" or a "micro-reinforcement".

The "macro-reinforcement" is accomplished by combining a woven fabric media with an ion exchange material leading to a composite membrane. This type of reinforcement limits the minimum thickness of the membrane because the ion exchange ionomer material must fully encapsulate the reinforcing support.

The "micro-reinforcement" is accomplished by combinations of a non-ionically functional microporous media with ion exchange material. Micro-reinforced composites differ from macro-reinforced composites in that the membrane voltage drop is no longer dictated by the need to satisfy mechanical requirements. Macro-reinforcements are generally visible to the naked eye, micro-reinforcement may not be.

Through the use of micro-reinforcement, several recent papers [39-42] have described the use of Gore-Select™ membranes in fuel cells. They result in a translucent structure with no visible evidence of any micro-reinforcement. The different steps of the fabrication of these reinforced composite membranes were not disclosed. The ionic conductivities, water content and hydraulic permeability, shrinkage, tensile strengths, chemical and dimensional stability, thermal stability and resistance properties were studied [39-42].

The low ionic conductivities of the reinforced membranes compared to those of Nafion® and Dow® membranes (Fig. 4) may indicate that they will not allow high proton conductivity. On the other hand, for the same EW, the reinforced membranes display the same water uptake as the unreinforced Nafion®. For the same EW, the ionic conductivity of Nafion® 117 (200 μm) is similar to that of Nafion® 112 (60 μm). It was claimed that the combination of reinforcement and thickness provides high membrane conductances (80 S/cm² for a 12 μm thick membrane (900 EW) at 25°C) and improved water distribution in the operating fuel cell without sacrificing longevity or durability. Such a conductance is particu-

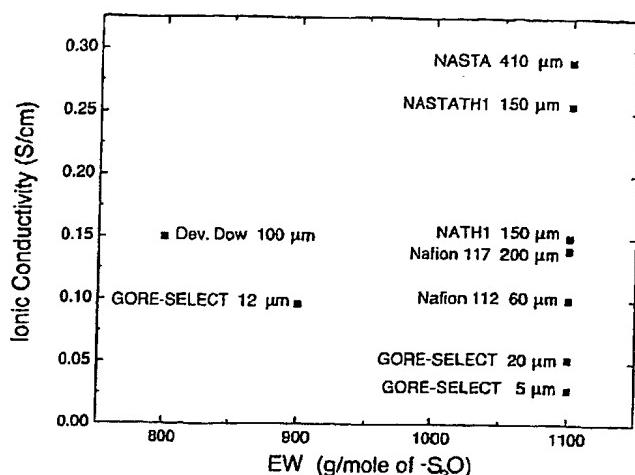


Fig. 4. Ionic conductivity (S/cm) for various Gore-Select, Dow, Nafion membranes and Polytechnique membranes (NASTA, NATHI, NASTATHI).

larly high when compared to that of Nafion[®] 112 (7 S/cm² for a 60 μm thick membrane (1100 EW) at 25°C) or to that of Dow[®] membrane (15 S/cm² for a 100 μm thick membrane (800 EW) at 25°C) (Fig. 5). The high conductances values of the reinforced membranes are due to the thickness of these membranes. The low ionic conductivity of the reinforced membranes is probably due to the presence of PTFE. These results indicate that the reinforced membranes may not have higher conductivity than unreinforced Nafion[®] or Dow[®] membranes. This reinforcement does not, of course, change the intrinsic chemical properties of the membrane (the conductance change is due to the thickness). Only the mechanical properties (shrinkage upon dehydration and membrane tensile strengths) and the hydraulic permeation dramatically change. The hydraulic permeability of the 20- μm -thick 1100 EW Gore-Select membrane is about 4 times as great as the 200- μm -thick, 1100 EW

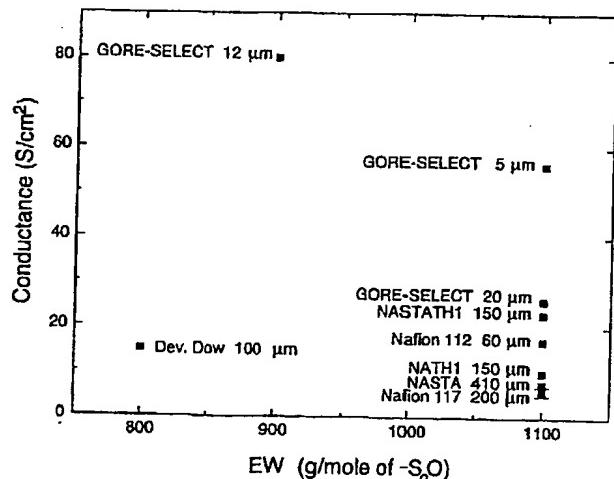


Fig. 5. Conductance (S/cm²) for various Gore-Select, Dow[®], Nafion[®] membranes and Polytechnique membranes (NASTA, NATHI, NASTATHI).

Nafion[®] 117 membrane. The membrane shrinkage upon dehydration of the 20 μm thick, 1100 EW Gore-Select membrane is also one quarter that of the 200- μm -thick 1100 EW Nafion[®] 117. In the dried state, Nafion[®] 117 and Gore-Select tensile strengths were found to be similar, but upon hydration, the Nafion[®] 117 loses over one-half its strength while the loss in the hydrated membrane is quite modest. These results are not rather surprising because of the hydrophobicity of the PTFE to water. It would be interesting to study the effect of the membrane tensile strengths upon the thickness of the reinforced membranes and the equivalent weights. These results may be correlated to their hydraulic permeability. This technology of reinforcement must be used for other membranes, and must also be developed elsewhere.

Thus, new very thin (5-20 μm) types of reinforced composite perfluorinated polymer electrolyte membranes, Gore-Select[™], have been tested for fuel cell applications [39]. Membranes of several thicknesses with carbon composite cathodes catalysed with 0.2 mg Pt/cm², were tested on 5 cm² fuel cell hardware. Platinum loading of the anode was not indicated. Hydrogen/air was used as the gas at the anode/cathode at pressures of 2.8/4.2 atm. The anode/cathode humidifiers were set at 105/80°C. From the polarisation curves for a 0.20 mg Pt/cm² catalysed 900 EW membrane 12- μm -thick at various reactant pressures for a cell temperature of 80°C, the cell yielded about 0.8 W/cm² at higher pressures and 0.45 W/cm² at a low pressure (1.2 atm.) of the cathode. It was claimed that it is possible to realise a non-humidification system with those membranes on a larger scale. Good water transport was also indicated due to a lack of increase in cell resistance with current density. These various fuel cell performance results have not been compared to those using unreinforced Nafion[®] of the same thickness. The reinforced membranes are, of course, more hydrophobic than the conventional Nafion[®]. It may be interesting to investigate if the low resistance is due to the high reinforcement of the membrane (which is very thin) or to its water transport ability. It is well established that, for all types of membranes, the lower equivalent weight enhances water transport ability. But, it does not seem that reinforcement has a beneficial effect on water transport. As an example, the hydraulic permeation (3.3) of the EW 1100 Nafion[®] 112 (60 μm thick) was similar (at 3.7) to that of the EW 1100 Gore-Select (20 μm thick) with only one-third the thickness.

3.1.2. New cation exchange membranes based on Nafion[®] heteropolycompounds with and without thiophene

Up to now, the Nafion[®] membrane and the Dow[®] membrane have been the most effective advanced membranes suitable for use in practical systems. The Dow[®] membrane exhibits superior performance to that of the Nafion[®] 117 membrane. The major disadvantage of these membranes is their high cost, as indicated above. This is due to the long preparation process and to the thickness of these membranes. The work initiated at École Polytechnique (Montréal, Canada) is designed to achieve direct chemical synthesis of Nafion[®] membranes from Nafion[®] solutions containing other polymers such as polythiophene, and different heteropolyacids using a novel method of preparation [43, 44]. Membrane preparation consisted in evaporating of the Nafion[®] solution and

mixing it with the appropriate concentration of heteropolyacids (silicotungstic acid, phosphotungstic acid, phosphomolybdic acid, etc.) to produce various membranes. Thiophene was subsequently added to the above electrolytes to produce the other types of membranes. Membranes of various thicknesses (10–500 µm) were elaborated by evaporating different amounts of electrolytes in a glass beaker with 100% optically flat bottom. After evaporation of the solvent, the films were peeled off the beaker and washed with de-ionised water and then stored in de-ionised water.

Ionic conductivity, conductance and morphological characteristics studies were carried out on several membranes [43]. It was found that the ionic conductivities of the membranes elaborated with Nafion®, heteropolyacids and/or thiophene are higher than those of Nafion®. The ionic conductivities of the membranes fabricated with Nafion® electrolyte and silicotungstic acid with and without thiophene are 2.3 times higher than that of the Nafion® 117 membrane (Fig. 4). Their conductances are also higher than that of the Nafion® 117 membrane (Fig. 5). The improvement in the conductance and conductivity was attributed to the effect of STA introduced in the films during membrane fabrication. This is not seen in the case of the Gore-Select membranes, where the improvement in the conductances was attributed to the thickness of the reinforced membranes (see above). The water uptake of the Nafion®, Dow®, Gore-Select membrane and the membranes fabricated with Nafion electrolyte and silicotungstic acid are shown in Table 2. As it may be seen, the water uptake of the Dow® membrane is higher than that of the Nafion® 117. This is related to the chemical composition of the membrane and not to its thickness. Effectively, Nafion® 117 (200 µm) and Nafion® 112 (60 µm) which have the same chemical composition but with different thicknesses exhibit the same water uptake. The water uptake of the Nafion® solution and silicotungstic acid is 40% higher than that of Nafion®. This may indicate that the silicotungstic acid may modify the membrane chemical properties. As well, membranes fabricated with Nafion® 117 and silicotungstic acid (NASTA) enhance water transport. Similar results were obtained on other heteropolyacids. The improvement in conductivity, conductance and water transport of the membranes was attributed only to the presence of the STA. The mechanisms of the process of "pigmentation" of the membranes by the heteropolyacids are not known. The behaviour of these pigmented membranes in solid polymer electrolyte fuel cells is under active studies. Many other properties of these membranes may be investigated (tensile strength, shrinkage in dried and wet conditions, long term stability in fuel cell applications, etc.). For fuel cell applications, we may also determine if these improved membranes have absolutely zero electronic resistance. The chemical composition of the "pigmented" membranes may be determined and compare to that of the Nafion® 117 membrane. This may help to correlate the chemical composition of the membranes and their properties. The extent to which these membranes are more economically acceptable than the Nafion® 117 membrane in fuel cells may also be addressed. The behaviour of these membranes in Polymer Electrolyte Fuel Cells is the subject of our continuing study.

Table 2. Membrane water uptake

Membrane	EW	Thickness (µm)	Water uptake (%)
Nafion® 117	1100	200	34 ^a , 32 ^b
Nafion® 112	1100	60	34 ^a
Dev. Dow®	800	100	56 ^a
Gore-Select	1100	20	32 ^a
Gore-Select	900	12	43 ^a
NASTA	1100	410	48 ^b
NASTHI	1100	120	32 ^b
NASTATHI	1100	150	30 ^b

Expressed as percent of membrane dry weight

^a From [39]: J. Kolde et al., in Proceedings of "First International Symposium on Proton Membrane Fuel Cells", The Electrochemical Society, Meeting, Eds. S. Gottesfeld, G. Alpert, and A. Landgrebe, The Electrochemical Society, Inc. 188th, Oct. 1995, p. 193.

^b From B. Tazi and O. Savadogo, J. New Mat. Electrochem. Systems (submitted).

3.2. Partially fluorinated ionomer membranes

3.2.1. The first sulfonated trifluorostyrene membranes

The preparation of the monomer α , β , β -trifluorostyrene was first carried out by Cohen et al. [45] who reported its total synthesis. The poly- α , β , β -trifluorostyrene has been firstly synthesised by Prober [46]. The structure of the polymer is shown in Fig. 6. Hogdon has investigated firstly the sulphonation of α , β , β -trifluorostyrene with applications to structures and cells [47, 48]. From optimisation of reaction conditions, he has prepared a multiplicity of equivalent weight or different ion exchange capacity of both linear and crosslinked poly- α , β , β -trifluorostyrene sulphonic acids. He has shown that the extreme difficulty in sulphonating poly- α , β , β -trifluorostyrene was found to be caused by the beta-directing influence of the perfluorinated polyalkyl group attached to the aromatic ring [47].

Then, the preparation of sulfonated poly- α , β , β -trifluorostyrene was found to be more difficult task than that encountered in the preparation of the corresponding polystyrene or polystyrene-divinylbenzene sulfonates. These polystyrene-divinylbenzene sulfonate polyelectrolytes were invented before by D'Alilo (see for example [49–52]). The degree of the α , β , β -trifluorostyrene sulfonation was very dependent on the temperature of sulfonation and the concentration of chlorosulphonic acid. The linear - α , β , β -trifluorostyrene sulfonic acid was prepared by a direct combination reaction of the chlorosulphonic with the trifluorostyrene. Sulfone-crosslinked poly- α , β , β -trifluorostyrene sulphonic acid was prepared. The poly- α , β , β -trifluorostyrene sulphonic acid has been found to be totally resistant to oxidative modes of degradation, which cause drastic oxidative depolymerization of the polystyrene and polystyrene-divinylbenzene sulphonic acids. This is attributed to the substitution of fluorine in place of the benzyl-hydrogen atom of polystyrene leading to the added C-F bond strength required to resist the oxidation environments. Thus, it was claimed that the high stability of the fluorine atoms attached to the alkyl carbon atoms impacts oxidative and thermal stability superior to that exhibited by conventional ion exchange polymers such as poly-

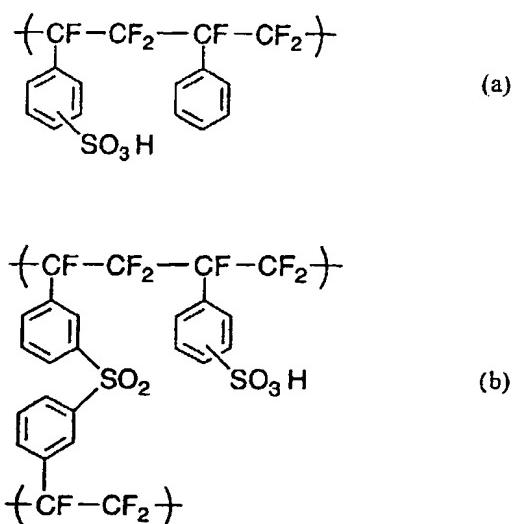


Fig. 6. General chemical structure of poly(trifluorostyrene) a) linear; b) crosslinked. From [19, 45-48].

styrene sulfonic acid, for example [48]. Their performance in fuel cells has been determined [53]. The use of a cross-linked structure greatly improves the dimensional stability, the membrane flexibility, and resistivity and the water ingestion and swelling. This may impart a cost reduction of the cross-linked of the polymer over the linear form. The chemical properties of these sulphonated trifluorostyrene membranes were shown to be very appropriate with membranes to be used in fuel cells. However, there are not a lot of data available in the literature on the behaviour of the membranes of the linear or cross-linked sulfonated polymer α , β , β -trifluorostyrene in fuel cell conditions. The limited use of these membranes in fuel cells may be related to their limited mechanical properties and/or chemical resistance in real fuel cell conditions. From the cell life as a function of operating temperatures for several membranes. The improved trifluorostyrene sulphonic membranes showed lifetimes of up to 3000 hours at low current densities and temperature of 50°C [54]. The effect of the cross-linked of the membrane on the fuel cell characteristics might be investigated systematically. The performance of these membranes at room temperature fuel cell operation for low power source would also be interesting. The study of these membrane properties elaborated with approaches like the Gore Technology may help in the understanding of their behaviour and of the effect of the method of fabrication in membrane lifetimes in real fuel cell systems.

3.2.2. The novel family of sulfonated copolymers based on the α , β , β -trifluorostyrene monomer

The longevity of the nonfluorinated BAM1G and BAM2G (Ballard Advanced Materials first and second generation of membranes, respectively) polymer-based membranes under practical fuel cell operating conditions were limited to approximately 500 hours (see Section 3.3.1.).

Based on the above work (see Section 3.2.1) [46,48] on the sulfonated α , β , β -trifluorostyrene membrane, a novel family of sulfonated copolymers incorporating α , β , β -trifluorostyrene and a series of substituted- α , β , β -trifluorostyrene comonomers provided the group of materials referred to as BAM3G (Ballard Advanced Materials third generation of membranes) [19,55,56]. The preparation scheme of the BAM3G and the general structure of this family of membranes are shown in Fig. 7. The water content of a series of these newly developed polymers ranging from 375 to 920 EW is shown in Fig. 8. For comparison, those of Nafion® and Dow® are indicated. As may be seen, the percentage water content of the sulphonated BAM3G is much higher than that of Nafion® and Dow® membranes. This is attributed to the small values of the EW of the BAM3G membranes. The performance of the BAM1G, BAM2G and BAM3G was determined in a standard membrane electrode assemblies (MEAs) prepared using each of the above membranes with both anode and cathode catalyst loading of approximately 4 mg/cm² of platinum. These MEAs were then evaluated for fuel cell performance in an experimental size Ballard MK4 single-cell fuel cell with an active area of 50 cm². The cells were operated on air/hydrogen at 24/24 psig, 2.0 : 1.25 stoichiometry and at 70°C [19,55]. A comparison of the begin-

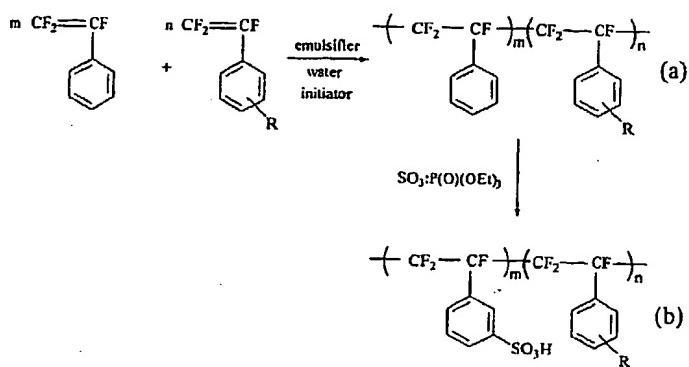


Fig. 7a) Preparation scheme of sulfonated BAM3G and b) General structures of these membranes. From [55].

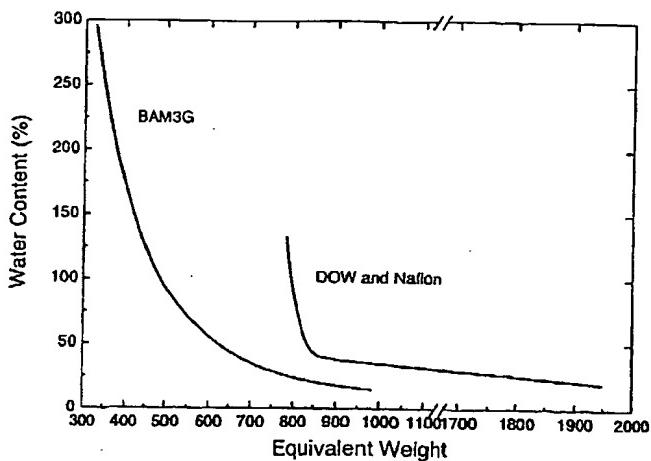


Fig. 8. Variation of the water uptake with equivalent weights of sulfonated a) BAM3G and b) Nafion®. From [55].

ning-of-life polarisation data for a representative sample of BAM1G, BAM2G and BAM3G is shown in Fig. 9. As may be seen, there is a clear improvement in performance efficiency in the development of BAM2G. The BAM3G maintained that high performance efficiency and increased its longevity. It was claimed that the longevity attainable from this new family of membranes is demonstrated in the lifetime plot of the commercial Ballard MK5 single-cell, which approached 15000 hours of performance in 1997. The BAM3G membrane exhibited performances superior to those of both Nafion® 117 and the Dow® membrane at currents above 600 A/ft² [55]. It was also claimed that they will be very low-cost (US\$5-15/ft²) polymer-based electrolytes and the expected production costs may be very compatible with those of fuel cell applications. Unfortunately, a great deal of the information related to the "intrinsic" properties of the BAM3G optimised parameters (thickness, ionic conductivity, conductance, exact chemical composition, mechanical strength, hydraulic permeation, etc.) is not available. At the same time, it will be interesting to study the

behaviour of the BAM3G membrane in other electrochemical systems (direct or indirect methanol fuel cells, water electrolysis using a solid polymer electrolyte, chloro-alkaline systems, electrosynthesis systems, etc.). It will also be interesting to determine the effect of membrane thickness on fuel cell performance. It will be a good idea to determine whether or not it is possible to realise a non-humidification system with those membranes.

3.2.3. Radiation-grafted membranes for fuel cell applications

The most significant first work carried out on the radiation grafting of polymers was achieved and reviewed by Chapiro [57]. The cation exchange membrane has been prepared by graft-polymerising α , β , β -trifluorostyrene onto the inactive polymer (fluorine-containing polymer) film, and then sulfonating the grafted film in different patents [58-61]. The grafted polymer membranes were obtained at a graft rate of 10 to 50%. Then, styrene or α , β , β -trifluorostyrene was grafted onto fluorine-containing polymers, followed by sulphonation of the grafted film. In particular, the membrane containing grafted poly(styrene sulphonic acid) and two low-density polystyrene membranes, poly(tetrafluoroethylene) and a copolymer of tetrafluoroethylene and hexafluoropropylene have shown similar conductivities to those of the Nafion® and Dow® membranes [62]. Many reports [19,63] indicate that the oxidation stability of these grafted foils is very limited. This makes them appropriate only for fuel cell applications. Only the membranes based on the poly(tetrafluoroethylene) backbone showed some promise as a candidate material.

It has been claimed that another approach using the simultaneous and pre-radiation grafting of monomers onto a base polymer film, and subsequent sulphonation of the grafted component, could be a viable method for synthesising stable proton conducting membranes [64-66]. These membranes were prepared in different steps based on fluoropolymer films, such as poly(tetra-fluoroethylene-co-hexafluoropropylene), FEP, or poly(ethylene-alt-tetrafluoroethylene), ETFE. In a first step, these polymers are pre-irradiated using an electron beam or gamma irradiation source. In a second step, the pre-irradiated films were grafted by exposing them to solutions of styrene and other radically polymerizable monomers to form hydrophobic, non-conducting grafted films, FEP-g-PS or ETFE-g-PS. Divinylbenzene (DVB) and triallyl cyanurate (TAC) were added as crosslinkers (XL) to the grafting mixture [67,68]. In the last step, the grafted films are sulphonated using chlorosulphonic acid. Fig. 10 shows the idealised structure of the grafted and sulphonated membrane obtained from ETFE. It was observed that: a) the chain scission increases with the irradiation dose in all cases except for ETFE irradiated under N₂ atmosphere; b) the chain scission is greater for γ -irradiated samples than for electron beam-irradiated samples, especially when irradiation occurs in air or oxygen; c) crosslinking can occur when ETFE is irradiated in a relatively good quality "oxygen-free" inert atmosphere. Based on different experimental results, it was concluded that the appropriate choice of base polymer film type, irradiation type and processing parameters can minimise the chain scission reactions during sample irradiation.

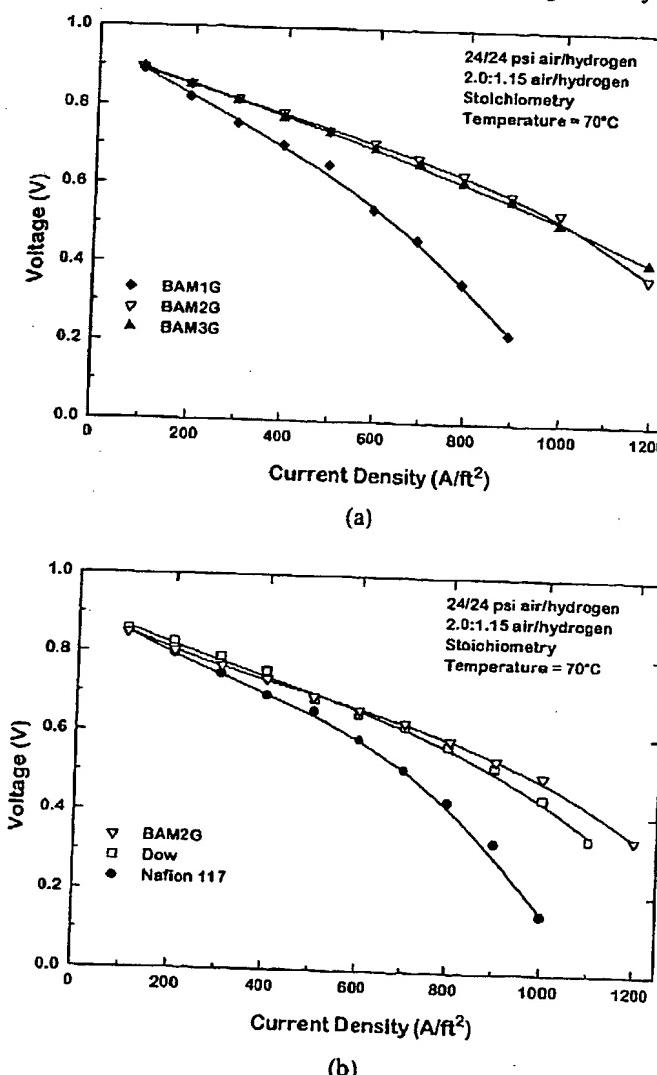


Fig. 9. Comparison of the beginning-of-life polarisation data for a representative sample of each BAM1G, BAM2G, BAM3G, Dow® and Nafion® 117. From [55].

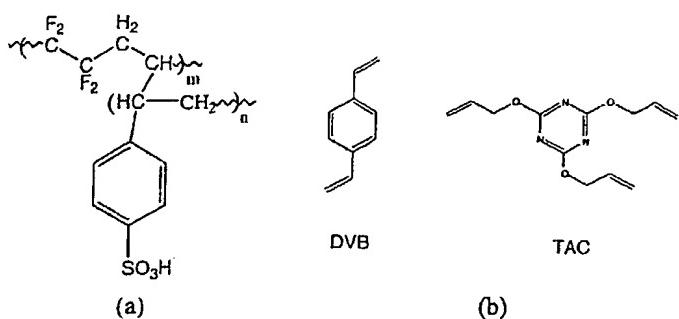


Fig. 10. General structure of the polystyrene grafted and sulphonated ETFE (ETFE-g-SPS). From [69].

Fuel cell performance investigations of the membranes were performed in a circular design and an active area of 28.3 cm^2 at 60°C or less (Fig. 11). The electrodes were based on carbon-cloth gas-diffusion electrodes (ELAT-type, Pt 0.6 mg/cm^2) modified by sputtering a layer of 0.2 mg/cm^2 Pt on the active layer and by impregnating them with soluble Nafion® (ca. 0.6 mg/cm^2). It was indicated that the membrane and the electrodes were individually inserted into the cell fixtures during cell assembly. Hydrogen (99.99%)/oxygen (99.5%) were used as the gases at the anode/cathode at atmospheric pressure. Hydrogen was passed through a water bath, which was kept at 20°C higher than that of the dual cell. No information was available for the oxygen humidification. This membrane electrode assembly was different from what is classically used where the membrane is pressed between the electrodes. At the same time, the modification of the electrodes by impregnating them with soluble Nafion®, of course, may indicate that the Nafion® has some effects on the improvement of the fuel cells based on grafted materials. It would be interesting to

determine the characteristics of the fuel cells based on these membranes with and without impregnating the electrodes in Nafion® solution. Study of the stability of these membranes in fuel cells at room temperature may indicate if they are also well suited for use in low power fuel cell systems. At the same time, it is worth studying the crossing of methanol through these membranes. It was found that: a) uncrosslinked membranes have lower resistance than cross-linked ones, for only a few hundred hours under fuel cell operating conditions [60]; b) the crosslinked membranes with DVB have a rather high resistance, but very good stability, whereas the membrane prepared using TAC has a low resistance which increases considerably with time. The most important problem with these membranes may be their stability in fuel cell systems. It seems that these membranes cannot be used at above 60°C . Also, based on results published elsewhere [63], it may be conclude that these membranes must be optimised before their use in practical systems. This method of preparation is, however, of great interest for the industrial preparation of modified polymers and membranes.

3.3. Non-fluorinated ionomer membranes

3.3.1. General considerations

Most efforts to develop high temperature proton conductors have involved hydrated inorganic oxides as O^{2-} -conducting ceramic electrolytes based on yttria-stabilized zirconia (YSZ). The conductivity is in order of $0.1 (\text{ohm.cm})^{-1}$ at 1000°C and it may not be used efficiently in fuel cells operating below that temperature. Further, for electrochemical systems operating in $100-200^\circ\text{C}$ range, these electrolytes may not be used without incurring high resistance losses. Thus, some engineering polymers which may support this temperature range and corrosive environments must be developed.

The leading type of solid polymer electrolyte proton conductor, the perfluorinated alkane membranes, is not sustainable for use at elevated temperature under steam, and under severe oxidising and reducing conditions. Studies of solid electrolyte properties have shown that the range of high temperature polymers has become quite large [70-74], but those which may exhibit exceptional thermal, hydrolytic or general chemical resistance are: a) aromatic polyesters, polyesters, polybenzimidazoles, and some of the polyimides which are stable at 200°C ; b) polyphenylene sulphides, polysulphones, poly(arylether sulphones), various polyketones, and some of the polyimides which are stable at 300°C .

Membranes based on hydrocarbon-type polymers were first developed at the General Electric Research Laboratories [19]. Specially, the phenolformaldehydes first described by Adams and Holmes [75,76] in 1935 and additional co-polymers such as the crosslinked polystyrene-divinylbenze sulphonic acids invented in 1944 by D'Alelio [49-52]. The chemical structures of these membranes are shown in Figs. 12 and 13. It has been indicated that the degree of sulphonation was difficult to control from batch to batch and the phenolformaldehydes yielded mechanically weak membranes with little resistance to hydrolysis due to the sulphonic acid groups [19]. The non-fluorinated poly(phenylene oxide) polymer

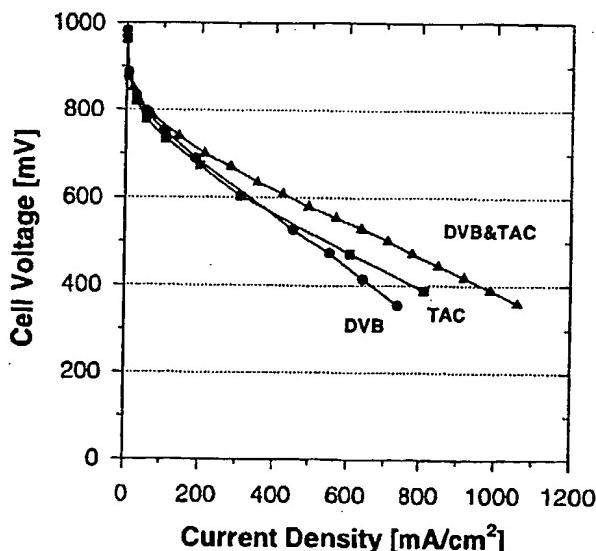


Fig. 11. Polarisation characteristics (after 70 h of continuous operation) of cells with differently crosslinked membranes (as indicated). $T = 60^\circ\text{C}$, H_2/O_2 1 bar. From [69].

was chemically modified to enhance both its mechanical and chemical properties [77-79] in view of their application in fuel cells. Some other different polymeric materials may be considered for the development of membranes for electrochemical systems: liquid crystal aromatic polyesters, polybenzimidazoles, polyimides, polyphenylene sulphides, polysulphones, poly(arylether sulphones), polysulphones, and various polyketones.

The main problem with the hydrocarbon-based membranes is that their chemical stability is poorer than that of perfluorinated polymers such as Nafion® due to their lower C-H bond dissociation enthalpies [47]. The attack of the tertiary benzilic group may be caused by the hydroperoxide radical formed according to the reaction of molecular oxygen with a hydrogen atom [53]. Due to the auto-oxidation of the hydrocarbons, the lifetime of the fuel cell using hydrocarbon-based membranes is less than that of fuel cell based on Nafion®. This lifetime may increase when the fuel cell using hydrocarbon-based membranes operates at low temperature (near room temperature).

3.3.2. Sulphonated poly(phenylquinoxalines), poly(2,6-diphenyl-4-phenylene oxide), poly(arylether sulphone) or poly(2,6-diphenylol)-based membranes

Ballard Advanced Materials have developed these membranes and those indicated in 3.2.2 over the last ten years through three generations of polymers [55]. The first generation of polymers referred as BAM1G were based on poly(phenylquinoxaline) (PPQ) polymers. They were synthesised by standard condensation polymerisation techniques [55,56,80]. With a view to facilitating the introduction of subsequent ion-exchange functionality, the PPQs were modified by the addition of bridges to increase flexibility in either the tetrakones and/or the tetraamine or both. Then, the preparation and polymerisation of single-Monomer PPQ was achieved. Subsequently, using chlorosulphonic acid, it was claimed that high yield and reproducible sulphonation reactions have been achieved which resulted in different levels of sulphonic acid content and hence different equivalent weights (EW).

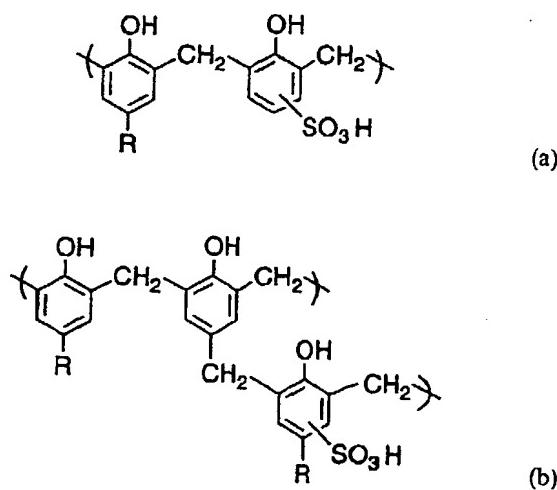
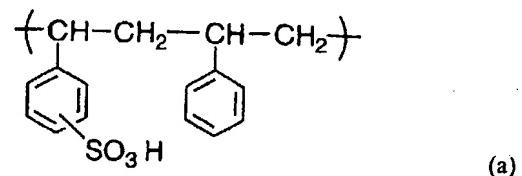
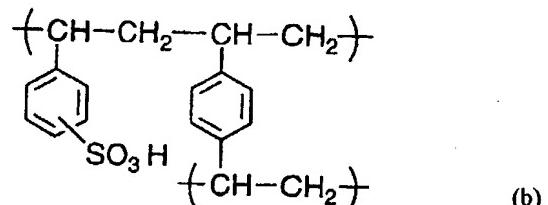


Fig. 12. General chemical structure of phenolformaldheyde: a) linear, b) cross-linked. From [19,75,76].



(a)



(b)

Fig. 13. General chemical structure of sulphonated polystyrene-divinylbenze sulphonic: a) linear, b) cross-linked. From [19] and G. D'Alelio, U.S. Patent 2,340,007 (1944).

It has also been claimed that the fuel cell performance achieved in general from BAM1G membranes of 390-420 EW is comparable to that of the commercially available perfluorosulphonic acid membranes [55]. After many iterations of EW, thickness and polymer structures variants, it was shown that the BAM1G membranes in an operating fuel cell when run at a constant 500 amperes per square foot (ASF), the average time before failure was approximately 350 hours. This is particularly low in comparison with Nafion® membranes, which show a lifetime of more than ten thousand hours [28]. It appeared unlikely that the BAM1G membranes could offer a real challenge to perfluorosulphonic acid membranes. To overcome this problem, a second generation of polymers referred to as BAM2G was developed. The polymers were prepared from poly(2, 6-diphenyl-4-phenylene oxide) [55] or poly(arylether sulphone).

The variation of the water content in the BAM membranes as a function of EWs ranging from 375 to 920 EV is already shown in Fig. 8. As may be seen and indicated above, the water content increases as the equivalent weight decreases. It may be seen in the same Fig. 8 that, for the same EW, the water content of the BAM membranes is higher than those of the Nafion® 117 membranes. This is an indication that the hydration process has improved in the BAM membranes relative that in the Nafion® membranes. Consequently, better water management must be facilitated with the BAM membrane relative to the Nafion® membranes. The percentages of water contained in the sulphonated BAM membranes rises exponentially below approximately 410 EW.

The polymerisation of 2,6-diphenylol resulted in a P_3O , which was sulphonated to P_3OHO_3H . The variant of the P_3O was submitted to bromination which gave P_3OBr followed by its sulphonation to P_3OBrSO_3H . The structures of these polymers are indicated in Figs. 14 to 16. The membrane electrode assemblies produced from these membranes were analysed in the same fuel

cell hardware under identical operating conditions (Fig. 9). They were unable to provide more than 500 hours of continuous running time at 500 amperes per square foot. To achieve fuel cell longevity, the third generation of BAM membranes based on perfluorinated backbone was developed (see 3.2.1). The poly(arylether sulphone) was also prepared and sulphonated. No behaviour of the sulfonated polysulphone membranes was shown. The behaviour of these membranes will be discussed in section 3.3.6).

3.3.3. Acid doped polybenzimidazole as a polymer electrolyte for methanol fuel cells

It is well established that the conductivity of the perfluorinated ionomer membranes currently used in polymer electrolyte membrane cells depends on the presence of water to solvate the protons generated by the ionisation of the sulphonic acid groups. When such polymers are subjected to temperatures above 100°C at atmospheric pressure, dehydration occurs, and conductivity decreases significantly [81,82]. It has been shown that, for a proto-

type Direct Methanol Fuel Cell (DMFC), the presence of methanol crossing over was responsible for the decrease in cathode potential by at least 100 mV [83,84]. From the investigation of the methanol diffusion in Nafion® [85], it was concluded that methanol readily transports across perfluorosulphonic acid membranes, and the investigation of new membrane systems for DMCS was suggested.

Up to now, it has not been possible to achieve an anodic current density of 600 mA.cm⁻² with less than 300 mV overpotential for methanol oxidation. This may be due to several problems: a) the self-poisoning effect due to strong CO-adsorption on Pt-based anodes; b) the low electrocatalytic activity of the anodes, which may increase at higher operating temperatures; and c) the high degree of methanol crossover through the Nafion® membranes. High temperature operation should enhance the methanol (MeOH) oxidation kinetics and should also depress the poisoning effect associated with strongly adsorbed intermediates, e.g. CO. An attempt at higher temperature (>100°C) has been demonstrated with humidified Nafion® as the electrolyte under pressurised condition [86-89] or with a polybenzimidazole (PBI) doped with phosphoric acid. Polybenzimidazole (PBI) is relatively low cost (US\$70-100/lb) and is a commercially available polymer known to have excellent oxidation and thermal stability. These properties prompted researchers at Case Western University to develop phosphoric acid-doped polybenzimidazole as a polymer electrolyte [81,90-99]. The general structure of the membranes is shown in Fig. 17.

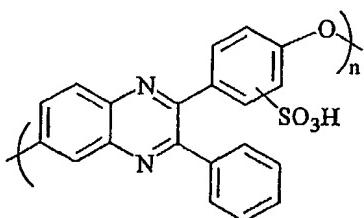


Fig. 14. General chemical structure of sulphonated poly(phenylquinoxalines). From [55].

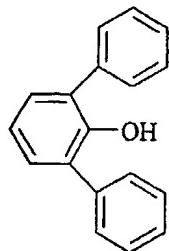


Fig. 15. General chemical structure of poly(2,6-diphenylol). From [55].

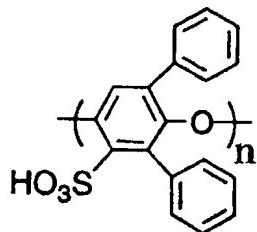


Fig. 16. General chemical structure of sulphonated poly(diphenil-1,4-phenylene oxide). From [55,77,78].

The polybenzimidazole films were cast in two manners (81). In the first case, they were cast from a solution of the polymer and then subsequently doped by immersion in a solution of 11 M H₃PO₄ for several days [81,99]. The doping level was typically five H₃PO₄ molecules per repeat units in a polymer-suitable solvent. Films formed in this manner were referred as type I films. In the second fashion, they were cast from a polymer and phosphoric acid in a suitable solvent. They are referred as type II membranes. In this case the sample preparation is greatly shortened because the films as cast are already doped. The typical doping level was six H₃PO₄ molecules per repeat unit in the polymer. The typical thickness for the different films was 0.0075 cm (3 mil). It was shown that the conductivity of type I membranes increases with increasing acid content, relative humidity and temperature. The conductivity ranges between 0.01-0.04 S.cm⁻¹ for temperatures between 130 and 200°C and relative humidities of 0.04-0.4. For the type II membranes, the conductivities are higher than those of the type I membranes. At temperatures above 150°C, the conductivity of type II membranes is similar to that of Nafion® at 80°C and 100% Rh. For 3-mil-thick films, the fuel cell resistance with type II is

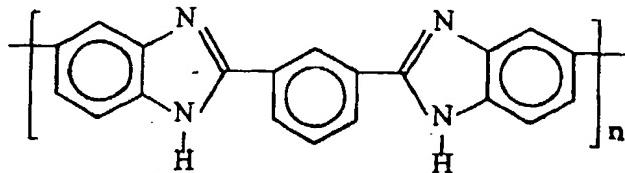


Fig. 17. A representation of the general chemical structure of polybenzimidazole.

0.1-0.2 $\Omega \cdot \text{cm}^2$. They have shown that the methanol crossover through doped PBI membranes (type I) was at least ten times less than that observed with Nafion®. It was claimed that the electro-osmotic coefficient of water drag determined under different conditions (temperature, humidity and current density) was essentially zero. Then, it was anticipated that the water balance problems should not appear with fuel cells using PBI membranes.

The fuel cell performance was performed using single cells 1 cm^2 in area in PTFE hardware supported by two stainless steel end-plates [99]. Oxygen/methanol was fed to the cathode/anode. The oxygen humidifier was set at room temperature. The methanol was introduced into the anode compartment in the form of vapour after vaporisation of the methanol/water mixture. The fuel cells were operated at the atmospheric pressure of both reactants. The anode/cathode catalyst was formed of platinum-ruthenium alloy/platinum black at loadings of 4 $\text{mg} \cdot \text{cm}^{-2}$ [96]. The direct methanol/oxygen fuel cell polarisation curves for type I and type II membranes are shown in Fig. 18 at a temperature of 200°C, atmospheric pressure and oxygen humidified at room temperature. The anode feed was 1:2 methanol: water by mole. The open circuit potential and the potential over a broad range of current density increase as the cell temperature increases. The increased performance with increasing temperature was attributed to lower methanol crossover and higher electrolyte conductivity. At 250 $\text{mA} \cdot \text{cm}^{-2}$ the voltage gain was approximately 75 mV over the 150-200°C range temperature.

For direct methanol fuel cells, the type II cell produced 0.21 $\text{W} \cdot \text{cm}^{-2}$ at 500 $\text{mA} \cdot \text{cm}^{-2}$, as compared to 0.16 $\text{W} \cdot \text{cm}^{-2}$ for the cell with the type I membrane at 150°C with a rather high catalyst loading (4 mg/cm²). But the mechanical properties of the type II membranes were found to be poorer than those of the type I membranes. For the fuel cell operating at 150°C with a type II membrane, a tolerance to 1% CO in H₂ was found due to the lower CO adsorption at this temperature [99]. After investigating on the thermal stability of PBI doped with phosphoric acid up to 600°C, it was concluded that this membrane is adequate for use as a PEM in a high-temperature fuel cell. Then, using H₃PO₄-doped polybenzimidazobenzonaphthalimides (PBPAs) which exhibit excellent thermal and mechanical properties [100].

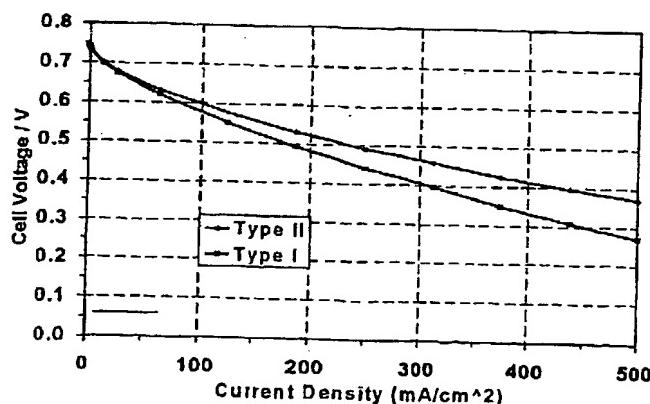


Fig. 18. Direct methanol/oxygen fuel cell polarisation curves for type I and type II PBI membranes. From [99].

order of magnitude the methanol crossover rate was measured in comparison to that with Nafion®. However, their long-term stability in a fuel cell operating condition must be studied. The methanol crossover is still very high, which can particularly affect the cathode performance for the oxygen reduction at low Pt loading. On the other hand, until now, the PBI membranes have not been doped by acids other like sulphuric acid. It will also be indicated that the PBI membrane has a similar structure the BAM1G membranes developed by Ballard Advanced Materials for SPEM fuel cell and their average time before failure was 350 hours. This is an indication that those membranes may not be appropriate for sulphuric acid doping. Despite the low methanol crossover rates for the H₃PO₄/PBI system, it is still of considerable importance to investigate new membrane systems if we want to avoid any cathode performance losses due to methanol crossover. These studies may also be extended to other polymers like the polybenzimidazobenzonaphthalimides (PBPAs) which exhibit excellent thermal and mechanical properties [100].

3.3.4. Sulphonated polyimides membranes

These sulphonated polyimides are based on 4,4'-diaminobiphenyl 2,2'-disulphonic acid (BDSA), 4,4'-oxydianiline (ODA), 4,4'-oxydiphthalic anhydride (OPDA) and 1,4, 5,8-naphthalene tetracarboxylic dianhydride (DNTA). Their general chemical structures are shown in Fig. 19. These monomers and solvents were obtained from commercial solvent. The co-polymer synthesis was achieved in two ways according to a procedure reported elsewhere [101-104]. The first way was based on the phthalimide-five-member imide (BDSA), OPDA and ODA) at 200°C and the second way was based on the naphthalimide-six member imide ring (BDSA, DNTA and PDA) at 160°C. The membranes of the sulphonated polyimide were obtained by casting on a glass plate from the polymer solution and then evaporating the solvent [102]. Swelling measurements, ion-exchange capacity, small-angle neutron scattering and full cell experiments were performed on these membranes. Their performance in fuel cells was compared to that of commercially perfluorinated ionomers e.g. Nafion® 117, having the same thickness. It was found that the water content or water uptake of membranes at 25°C for the phthalic and naphthalenic sulfonated polyimide membranes are 26% and 30% respectively. The water content obtained for Nafion® membranes in the same conditions was 20%. However, it was found that with the Nafion® 117 membrane, the water content increases exponentially with the temperature [103, 104] while the degree of swelling is almost constant when the temperature increases for sulphonated polyimide. It

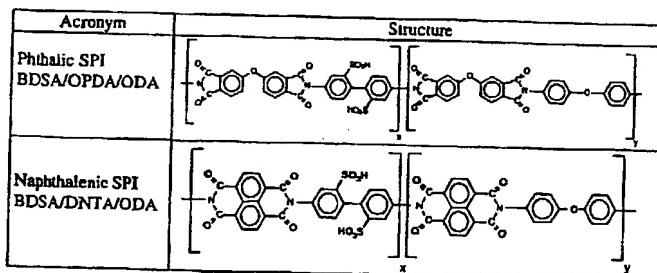


Fig. 19. General chemical structure of polyimide. From [102].

was also claimed that the sulphonated polyimide membranes were 3 times less permeable to hydrogen gas than Nafion® membranes.

The membrane performances were tested in H₂/O₂ fuel cells at 70°C with an active area of 20 cm² [103]. The electrodes were based on carbon cloth gas diffusion electrodes with a platinum content of 0.35 mg.cm² (E-TEK, USA) and impregnated with a Nafion® solution of to 0.8 mg/cm². The electrodes were set up with the polyimide without hot pressing. The H₂/O₂ humidifiers were water baths at the same temperature as the fuel cells. The gas pressures were not indicated. A Nafion® 117 membrane was used as a reference for the analysis of the results. The three membranes used (phthalic, naphthalenic polyimides and Nafion® 117 membranes) have the same thickness. The polarisation curves were recorded when the steady state conditions were obtained (≥ 24 hours). The polarisation curves are shown in Fig. 20 for the three membranes. The curve obtained with the naphthalenic membrane is almost similar to those obtained with the Nafion® 117 membrane. In particular, at high current densities ($> 0.8 \text{ A/cm}^2$), the naphthalenic membrane performs better than the Nafion® 117. In contrast, the curve of the phthalic membrane is under those of the naphthalenic and Nafion® 117 membranes. Since the membrane electrode assembly was not created by pressing at high temperature, the ohmic losses observed were high. However, the comparison of the membrane performances was made in the same experimental conditions. This is not the case for the work on several new membranes of the performances, which were not compared to those of a reference membrane. From lifetime measurements performed on a 175 µm phthalic polyimide or a Nafion® membrane and a 70 µm naphthalenic sulphonated polyimide at 60°C, 3 bar pressure for H₂ and O₂ and under a constant current density, it was found that: a) the membrane based on phthalic structure broke after 70 hours leading to a local combustion of the membrane; b) the membrane based on the naphthalic polyimide was stable over 3000 hours. The degradation of the phthalic-sulphonated polyimide was attributed to the hydrolysis of the sulphonated polyimide sequence

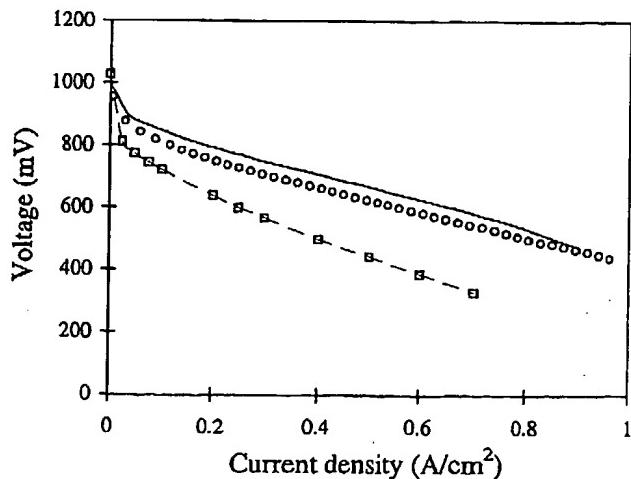


Fig. 20. Polarisation curves recorded at 70°C and $p_{H_2} = p_{O_2} = 4$ bars for the phthalic (□) and naphthalenic (○) polyimide membranes and the Nafion® 117 membrane as a reference (solid line). From [102].

leading to chain scissions, which is responsible for the loss in mechanical properties. It was claimed that this phenomenon was not described for naphthalene polyimide membranes. However, the stability of the naphthalenic polyimide membranes must be evaluated with experiments that will include the evolution of the mechanical properties and the polarisation of the membranes in fuel cell conditions. The study of the surface properties of fluorinated polyimides exposed to VUV radiation and atomic oxygen may help us understand the stability of these polymers. It will also be interested to apply this approach method of sulfonation to some novel high-molar-mass poly(ether imide) which general chemical structure is shown in Fig. 21 [105].

3.3.5. Styrene/ethylene-butadiene/styrene triblock copolymer

The styrene/ethylene-butadiene/styrene triblock polymer is a commercially available product (Kraton G1650) containing a saturated carbon centre block, which should be inert to the sulphonation reaction. These hydrocarbon-based block polymers have been considered because they are less expensive than Nafion® and may exhibit a rich array of microphase-separated morphologies, with which it might be possible to minimise the properties of Nafion®. The structure of the polymer is shown in Fig. 22 [106-108]. This membrane has been developed by DAIS Company, (USA).

The typical casting solvent of the sulphonation process is rich in n-propanol, which should preferentially solvate the sulphonated styrene blocks. It has been claimed that membranes with reproducible properties at a constant sulphonation were obtained. It was also indicated that the conductivities at sulphonation levels above 50 mole % of styrene units exceed that of Nafion® under similar measurement conditions. In particular, a sulphonation level of 60% was found to be a good balance of electrical and mechanical properties. The predicted lifetimes of DAIS-membrane-based fuel cells were 2500 h at 60°C and 4000 h at room temperature. The problem of low stability of the hydrocarbon-based-mcmbranes in fuel cells at high temperatures may be solved by using them in low temperature and low power fuel cell systems. For these low temperature fuel cells, no energy supply is necessary due to the heating involved. The water management and/or the membrane dehydra-

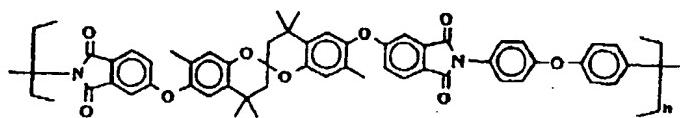


Fig. 21. General chemical structure of poly(ether imide). From [105].

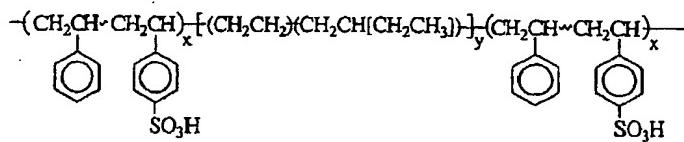


Fig. 22. Structure of partially sulphonated block polymer styrene/ethylene-butylene/styrene. From [106].

tion in low temperature fuel cells is less important than that in high temperature fuel cells.

The current-voltage curve of the DAIS membrane-electrode assembly based on the styrene/ethylene-butadiene/styrene triblock co-polymer in a flow-through cell is shown in Fig. 23. Compressed air was used as the oxygen source at the cathode, and commercial grade hydrogen at the anode at 40°C, atmospheric pressure and without humidification. The platinum loading of both the anode and cathode was approximately twice the necessary stoichiometric flow at peak power. The feature of this curve seems to be interesting because of the high open circuit at 0.95 Volt and the power at 0.5 V of about 200 mW/cm² at 40°C. But it would be very interesting to have the polarisation curve of the same cell using Nafion® 117 as a reference. At the same time, the study of the long-term stability of this low temperature fuel cell is necessary for its use in practical systems. In particular, it is important to know if the power of 200 mW/cm² at 0.5 V can be maintained in long-term utilisation.

3.3.6. Partially sulphonated poly(arylene ether sulphone)

These polymers display excellent mechanical properties, good thermal stability, toughness and excellent resistance to hydrolysis and oxidation [109-111]. The synthesis and characterisation of sulphonated poly(arylene ether sulphones) has been achieved [79,112]. Their chemical structure is shown in Fig. 24. Johnson *et al.* [112] demonstrates that the preparation of sulphonated poly(arylene ether sulphone) can be used to generate transparent and tough films. The sulphonation level is influenced by the water uptake and the magnesium counterions enhance the rubbery plateau and modulus. The properties of these membranes were not investigated in electrochemical systems.

The study done in reference [79] was based on the conversion of the temperature and oxygen resistant hydraulically stable aromatic polyethers, in particular poly(arylene ether sulphones) into

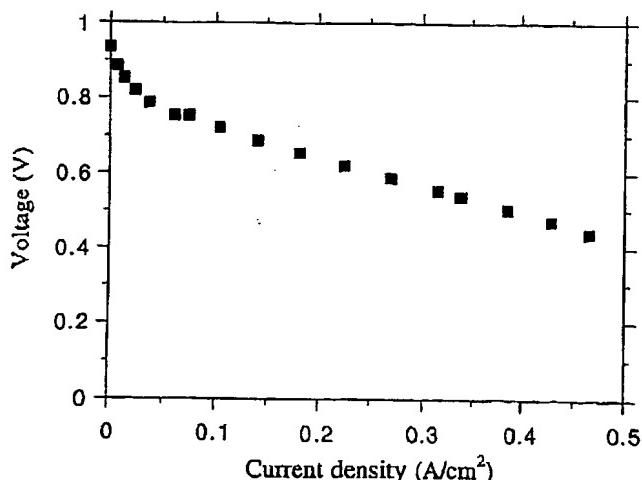


Fig. 23. Polarisation curve for a membrane electrode assembly derived from 60 Mol% sulphonated triblock polymer PEM and DAIS electrodes. From [106].

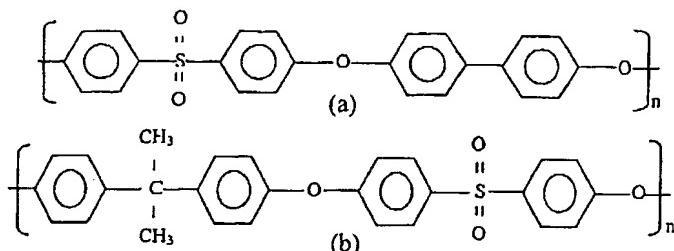


Fig. 24. General chemical structure of poly(aryl ether sulphones). From [79,110-117]: (a) Polysulphone (PSU); (b) Polyethersulphone (PES).

polyelectrolytes via functionalization of such polymers in a post polymerisation step.

For example, the evaluation of the poly(arylene ether sulphone)-based solid polymer electrolytes prepared by sulfonation of the commercially available poly(arylene ether sulphones) Udel® P-1700 (PSU) and Vitrex® PES 5200P (PES). They were purchased and used without purification. The polymers were dried in vacuum at 130°C for 8 hours, following procedures already described in literature [113,114]. The sulphonation process of the membranes was achieved either by the solution procedure [99] or the slurry procedure [114].

Thin films (about 50 µm thickness) of non-crosslinked membranes were prepared by casting polymer solutions in DMF (150 g/l or 300 g/l) on a glass substrate using a film-coating machine [115]. They were dried at 1 mbar and 150°C for eight hours.

The thickness, the specific resistance R, the permselectivity, the degree of swelling in water at 25°C and 80°C, the current/voltage plot in a water electrolytic cell and a short life time test at 25°C, 1 A.cm⁻² during 300 hours were determined [79].

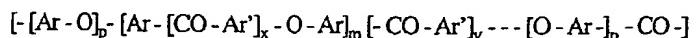
The properties of PSU polymers have been described elsewhere [116,117]. It was found that membranes cast from sulphonated PSU (Udel® P-1700) solutions were completely water soluble and impossible to characterise, of course, their resistance, permselectivity or swelling [79]. This is in agreement to the results obtained elsewhere [118]. These results showed that attempts to sulphonate at great than 29.5% resulted in H₂O soluble polymers. Even, the 29.5% sulphonated sample was soluble in hot water. In contrast, the non-crosslinked (Vitrex® 5200P) is very stable in water [79]. It was shown that the specific resistance decreases when the degree of sulphonation increases. This was attributed, of course, to the higher concentration of fixed charges inside the membrane. The specific resistance (*i.e.* 76 Ω.cm) of the highly sulphonated non-crosslinked membranes samples is in the range of that of Nafion® (*i.e.* 100Ω .cm). The type of Nafion® which was used as a reference and its thickness were not indicated. The permselectivity of the membrane increases when the sulphonation degree increases. The membrane with the higher degree of sulphonation exhibited the same permselectivity as Nafion® (90%). The uptake of water increases with the sulphonation degree. It increases by up 70% and for the highest sulphonated membrane, the

water uptake (74%) is at least 3 times higher than that of Nafion® (21%). The water uptake increases also more than 400% from 25°C to 80°C for the membranes prepared with a degree of sulphonation of about 90%. To decrease the membranes water uptake, crosslinked membrane has been elaborated during the casting process by reacting activated sulphonic acid, preferably N-sulfonyl-imidazole with diamines. In those conditions, only 50 mole% of sulphonic acid groups can be activated. The comparison of the properties showed that: a) the specific resistance of the crosslinked membranes are two times higher than that of the non-crosslinked (76 Ω.cm Vs 160 Ω.cm); b) its water uptake is 50% less of the non-crosslinked one (180% vs. 420%), and c) their permselectivities are similar (80% vs. 90%). Up to now, no fuel cell performance data is available. It is still of considerable importance to investigate the performance of these membranes in solid polymer electrolyte and direct methanol fuel cells. This may help in the understanding of the behaviour of several membranes for these systems.

A new sulphonation process for polysulphone PSU ionomers has been indicated [63,118-121]. It was reported that these polymers have been formed into membranes cross-linked by a new cross-linking procedure. The scheme of the sulphonation process is shown in Fig. 25. It was claimed that the membranes have a good thermal stability and good ionic conductivities, at moderate swellings rates. The fuel cell performance of the two sorts of Membrane Electrode Assembly (MEA) units was poor [63] (e.g. a maximum cell voltage of 0.400 V at 100 mA/cm² at 80°C). The MEA units were made either by a cold-pressing of the electrodes onto the membrane or by a hot-casting of an electrode material containing aqueous slurry, followed by evaporation of the water. The reasons for the limited performance were not explained. The comparison of the properties of these membranes to those of the other sulphonation processes may be of particular importance in the development of efficient membranes for electrochemical systems. The comparisons is necessary because one question arises: Is and/or how the sulphonation process may have some effect on the performance of the membranes in the fuel cell?

3.3.7. Partially sulphonated polyether ether ketone (PEEK) membranes

The structure of the polyether ether ketone is shown in Fig. 26 (PEEK). It is consisted of 1,4-disubstituted phenyl groups separated by any of a number of linkages of – O – and – CO – [122,123] - [O – (Ar) – O – (Ar) – CO – (Ar) –]n. The general formula of the aromatised polyether ether ketone is [123]:



where Ar is a phenyl group and Ar' may be a phenyl, naphthyl, biphenyl, anthryl or other aromatised groups. The value of x, n and m can be 0 or 1. The value of y may be 0, 1, 2 or 3 and that of p, 0, 1, 2, 3 or 4.

The electrophilic aromatic sulphonation of the polyether ether ketone was established in the literature [122,123]. The general concept of the sulphonation consists in dissolving the dried PEEK in concentrate sulphuric acid. The desired level of sulphonation being depending on the time and the temperature of the process. As an example, Bailey *et al.* [124] have sulphonated the PEEK by using the following steps: a) dissolution of 10 g of oven dried PEEK was dissolved in 100 ml of 96% H₂SO₄. The tan PEEK dissolved within 2 hours to give a deep red, viscous solution. The time and the temperature of the reaction were varied in order to achieve the desired level of sulphonation. The reaction was quenched by slowly pouring the acidic solution into one litter of distilled water. The precipitation of the polymer may appear instantly forming a continuous white string. In the last step, the polymer was extensively washed to remove the excess acid, and dried in a vac-oven at 100°C. The degree of sulphonation was determined via a combination of acid/base titrimetry and gravimetry [122]. Sulphonation levels between 20-75% were achieved by varying reaction time and temperature [122, 123]. The sulphonated polymer was obtained as solid white strands and droplets. It was converted into films by dissolving the polymer in DMF, casting the solutions in a crystallising dish, and evaporating the solvent to dryness. Films were hot-pressed to uniform thickness at 100°C and several thousand

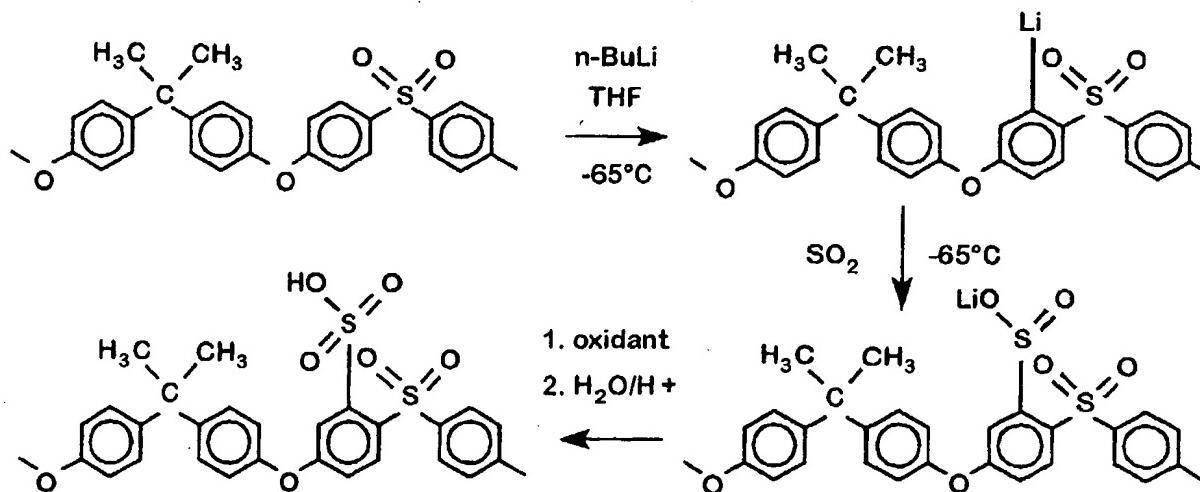


Figure 25. New sulphonation process of polysulphone polymers. From [63, 118-121].

psi. It has been shown that at 32% degree of sulfonation SPEEK (Sulfonated Polyether ether ketone) sample showed a resistance of $75 \Omega \text{ cm}$ at 81°C and at saturation its H_2O uptake was 47% by weight of the original dried film corresponding to a 25.6 H_2O molecules/sulfonic acid [122].

The performance of the SPEEK membranes was determined for water electrolysis. The following results were obtained: a) higher degrees of sulfonation enable modest improvements in current density: by doubling the density of ionic groups from 20 to 46.5% sulfonation, the current density at 2.00 V increased from 50 to 70 $\text{mA} \cdot \text{cm}^{-2}$; b) at low electrolysis voltages, the SPEEK at 65% sulfonation and the commercially available Nafion® 117 perform essentially the same. However, at higher voltages and current densities, the SPEEK membrane performance exceeded the Nafion® membrane; c) the coulombic efficiency of the electrolysis was above 90% at the highest voltages. Unfortunately, the membranes has swollen in a gel-like state. This may make them mechanically very fragile. The lifetime of such membranes in electrolysis systems can be limited due to the above behaviour.

The sulfonated polyether ether ketone membranes were also proposed as proton conductors in polymer electrolyte fuel cells [123]. Unfortunately, no fuel cell performance using SPEEK was available in this patent. As indicated above, the different steps of the polymer sulfonation and membrane casting were indicated and its performance for water electrolysis at 80°C was a cell voltage of 2.15 volt at $1 \text{ A} \cdot \text{cm}^{-2}$. The membrane resistance was 185 mohm. No correlation between the membrane properties and their thickness have been established. The equivalent weight of the SPEEK was not indicated and the comparison of its performance to that of Nafion® was not done in the same thickness basis. The Nafion® water uptake was also not indicated. Thus, the evaluation of the performance of the SPEEK in fuel cells is needed in a basis of systematic study of fuel cell characteristic upon membrane thickness and water uptake.

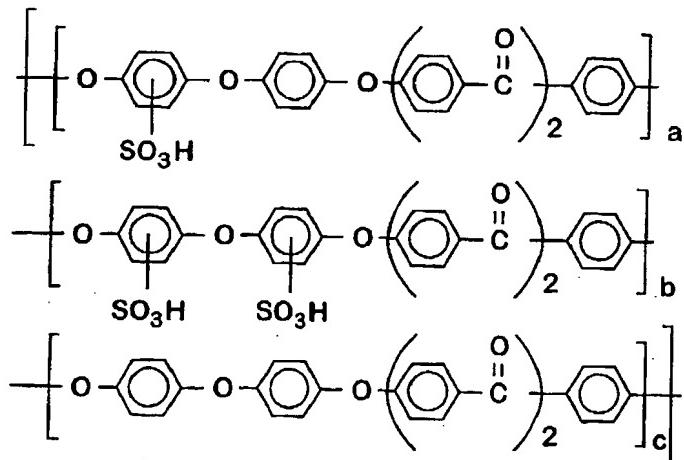


Fig. 26. General chemical structure of poly(ether ether ketone). From [119, 120].

3.3.8. Poly(benzyl sulphonic acid) siloxane (PBSS) based membrane

This membrane is based on organic-inorganic protonic polymer electrolyte (ormolyte-organically-modified silane electrolyte). The general structure of poly (benzyl sulphonic acid) siloxane is shown in Fig. 27 [125-128]. The synthesis was realised by the sol-gel process during different steps. It was based on the hydrolysis-condensation of the benzyl-triethoxylane precursor in a methanol solution containing water and triflic acid ($\text{F}_3\text{SO}_3\text{H}$). The steps of preparation are indicated elsewhere [127,128]. The polymer was sulphonated in dichloromethane solvent using chlorosulphonic acid (ClSO_3H). Several co-polymer compositions prepared from different proportions of the mixture of benzyl-triethoxysilane, n-hexyl trimethoxylane and ethoxysilane (e.g. different organically modified alkoxy silanes). Cross-linking was also performed in THF by hydrosilylation of silane groups with divinylbenze using devinyltetramethylsiloxane platinum complex as catalyst.

It was been claimed that the final inorganic-organic ion-exchange ormolyte has good thermal stability up to 250°C . A conductivity of $1.6 \times 10^{-2} \Omega^{-1} \text{ cm}^{-1}$ at room temperature was shown [127]. It has been claimed that these properties made them useful for direct methanol fuel cells. Up to now, no fuel cell performance data was given. It will also be interesting to study the methanol crossover in the membrane. Its chemical stability in practical fuel cell systems may be addressed.

3.3.9. Protonic electrolytes based on hydrogels

Besides studies on anhydrous proton polymer conductors [9-18], various groups have studied protonic conductivity in systems in which water solution of H_3PO_4 or H_2SO_4 was used as an additive to the polymer matrix [129-143]. Application of proton conducting polymeric electrolytes in various electrochemical systems including fuel cells has been discussed [144-146]. Studies on proton conducting polymeric electrolytes have been initiated by Armand *et al.* [147]. This interest is related to their expected high conductivity at ambient and sub-ambient temperature. An example is the poly(vinyl alcohol)- H_3PO_4 systems which conductivities exceeding 10^{-3} S/cm at ambient temperature [129]. Systems based on complexes of phosphoric acid with poly(ethylene oxide)-

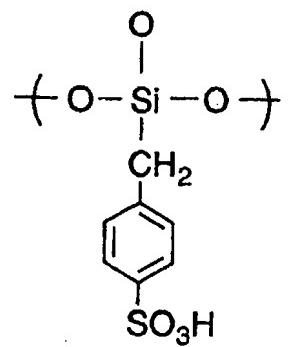


Figure 27. Chemical structure of poly(benzyl sulphonic acid) siloxane. From [19,127].

poly(methyl methacrylate) (PEO-PMMA) blends were described [132,134]. The polymer blends were prepared by thermal polymerisation of methyl methacrylate in the presence of high molecular weight PEO, followed by dissolution of a thermally prepared blend in acetonitrile. Phosphoric acid concentration varying from 5 to 50 mol % with respect to ethylene oxide molecular units was added as a proton donor to the electrolyte after homogenisation. It was shown that the mobility of protonic in the phase was comparable to that of liquid systems and the conductivity values of PEO-PMMA-H₃PO₄ exceed 10⁻³ S.cm⁻¹ at room temperature. It was claimed that this value is enough for application in fuel cells as a Nafion® substituant and in devices requiring high power current output [134]. It has been shown that the mixing of PEO with softer organic fillers, such as polycrylamide (PAAM) can inhibit crystallisation without impeding segmental chain motion and ionic mobility [135]. Thus, it has been found that the addition of poly(N, N-dimethyl-acrylamide) fillers increases ambient and sub-ambient temperature conductivities by about 1-2 orders of magnitude in comparison with the pristine oxymethylene linked poly(ethylene oxide)-LiClO₄ electrolyte [140]. It must be indicated that the main characteristics of these electrolytes are related to those of complexes of strong inorganic acids (e.g. H₃PO₄ or H₂SO₄) with polymers having basic groups of different basicity in a main or a side chain such as linear or branched poly(acrylamide) (PAM), poly(ethylene innine) (PEM), etc. [130,133]. This characteristic may, of course, affect their behaviour in practical systems. It has been indicated [148,149] that the conductivities of complexes of linear PAAM with H₃PO₄ or H₂SO₄ were in the range 5×10⁻⁴ to 5×10⁻³ S/cm at ambient temperature and 100°C respectively. It has also been shown that the conductivity of such membranes can be increased by at least one order of magnitude after humidification with moist gases [150]. Unfortunately they exhibit poor mechanical and chemical stability after humidification. It has been demonstrated that thin film proton conducting polymer gels based on PAAM matrix and agar with a H₃PO₄ additive exhibited reasonable mechanical strength and ambient temperature conductivities in the range of 10⁻³ to 10⁻² S/cm [151]. DSC measurements indicate that these protonic gels are stable up to 120°C. The values of these conductivities are higher than those obtained from many above non fluorinated membranes. However, their mechanical stability and conductivities are very dependant of their water content. Their water uptake is also not well determined in various conditions of operation. According to the available data in the literature, the conductivities of these systems are less than those of perfluorinated membranes at room temperature. It will be interesting to study their performance in practical fuel cell systems. In particular, the stability of these proton electrolyte conductors in practical systems must be studied in details.

4. CONCLUSION

Based on the results presented here, it may be concluded that the perfluorinated and the partially fluorinated ionomer membranes exhibited the best performance and highest longevity for some fuel cell systems applications. However, the high cost and/or the lack of high performance of the membranes may limit their use in all fuel cell systems. Even through many membranes are being

developed for electrochemical systems, in particular for fuel cell systems, there are enormous technological implications, as well as materials and manufacturing issues, which have to be continuously addressed: a) new manufacturing technologies for Nafion® have to be found and/or developed; b) alternative membranes found and/or developed, each membranes perhaps being developed for a specific electrochemical system and/or a specific power range; c) the development of alternative membranes to integrate new manufacturing technologies for membrane electrode assembly; d) the ultimate goal of membrane research which may be to avoid high cost membranes for transportation and low power fuel cell systems; e) consideration of the duration of service of the membrane in practical systems and its ease of production on a large scale at low cost.

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